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Use of sequential leaching, mineralogy, morphology and multivariate statistical technique for quantifying metal pollution in highly polluted aquatic sediments—A case study: Brahmani and Nandira Rivers, India

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ABSTRACT

The particle size distribution, geochemical composition and sequential leaching of metals (Fe, Mn, Ni, Cu, Co, Cr, Pb, Zn and Cd) are carried out in core sediments (<88 μm) from the Brahmani and Nandira Rivers, India. To confirm the contamination of downstream sediments by fly ash, mineralogical and morphological characterizations were carried out. High environmental risk of Co, Pb and Ni is due to their higher availability in exchangeable fraction. The metals like Zn, Cu and Mn represent an appreciable portion in the carbonate phase. Metals such as Zn, Pb, Cd, Co and Ni are associated with reducible phase may be due to adsorption. The organic bound Cu, Zn, and Pb seem to be second dominant fraction among non-lithogenous in Nandira sediments. Factor analysis data reveals that textural parameters, Fe–Mn oxy/hydroxides, organic precipitation and coal fly ash disposals, are individually responsible for the enrichment of heavy metals. The relationships among the stations are highlighted by cluster analysis to identify the contamination levels.

1. Introduction

Sediments transported by rivers, by and large, are the erosional products of the rock types exposed in the basin. River sediments provide a major sink for heavy metals in the aquatic environment by various physico-chemical processes such as precipitation, adsorption and chelation. The contribution of heavy metals depends on a variety of factors such as basin geology, physiography, chemical reactivity, lithology, mineralogy, hydrology, vegetation, land-use pattern and biological productivity. Besides the natural processes, additional influx of the solid wastes into the river sediments from the industrial activities and mining practices causes enrichment of heavy metals. The amount of influx of the waste material into the river system varies depending upon the intensity of these activities. Determination of total metal content in sediments provides important information about pollution level if the background concentration is known. However, to understand the mobilization of heavy metals and assess the bioavailability, the total concentration is not enough [1]. Therefore, it is vital to perform chemical partitioning studies of heavy metals in the sediments to accurately assess the toxic potential. The rivers Brahmani and Nandira, not only obtain sediments from natural sources but also receive enormous amounts of solid wastes from industrial activities in Angul-Talcher area, Orissa. Hence, an attempt has been made to study the heavy metals in the sediments of these rivers.

In India about 65% of total electricity is generated through the use of coal as fuel. Indian coal contains up to 55% ash and its combustion results in large amount of residual coal fly ash [2]. Presently about 110 million tones of coal-ash is generated in India [3] and by the year 2012 this is predicted to increase to 170 million tons per annum [4]. The physical and chemical properties of this industrial waste in general are quite variable as they are influenced by coal source, particle size, type of coal burning processes and degree of weathering. Coal fly ash is a mixture of metallic oxides, silicates and other inorganic particulate matter along with unburnt carbon. Apart from this, it also contains many trace metals. The leachability of these trace metals to surface waters is quite important. Trace metals, though present as a relatively small fraction in coal fly ash are of special interest due to their cumulative build up, long life, high toxicity to man, plants and animals through air, water and soil intake [5]. Ash contamination poses a serious threat to

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environment. Untrapped and air borne coal fly ash can get deposited over a vast surface of land water basins damaging and intoxicating the flora as well as contaminating the aquatic systems [6]. Since the rivers of our study area are carrying a substantial amount of coal fly ash from the thermal plants, the study has been extended to estimate the contribution of trace metals due to contamination of the same.

The risk assessment code (RAC) demonstrates that the metals in sediments are bound with different strengths to different fractions. The RAC assesses the availability of metals in solution by applying a scale to the percentage of sediments that can reduce metals in the exchangeable and carbonate fractions. With the aim of achieving a broder assessment of Brahmani and Nandira metal pollution in terms of ecological risk, a quantitative approach has been made.

2. Background

2.1. Geographical settings

The area under study is bound by 20°49′ and 21°6′N latitudes and 85°5′ and 85°26′E longitudes (Fig. 1). The river Brahmani along with its tributaries forms the major drainage in the area. This basin lies in an Indian shield, which constitutes pre-cambrian rocks such as granites, granite gneisses, quatzites, schists, amphibolites, pegmatites, khondalites and charnockites and gondwana rocks like shale, sandstone and coal, specifically in and around Talcher. The soil of the area varies from rich red loamy to gravelly detritus with a small patch of laterite. The elevation of the land surface ranges from 60 to 200 m above mean sea level [7]. The area enjoys a subtropical monsoon climate with an average annual rainfall of 1421 mm. The temperature varies from 6 to 46° C [8].

2.2. Anthropogenic setup of the basin

Availability of raw materials, perennial water supply from Brahmani–Nandira, ease of transport and free market conditions led to rapid growth of industrialisation in the study area. Intensive industrialisation and mining activity in the industrial belt of Angul-Talcher leading to solid and liquid waste disposal have created environmental problems pertaining to heavy metal contamination of Nandira River and ultimately that of Brahmani. The area is quickly emerging as a big source of coal and thermal power in the country. The major industries existing in the area include three power plants; Talcher Thermal Power Station (TTPS), National Thermal Power Corporation (NTPC), NALCO Captive Power Plant (CPP); a Fertilizer plant (FCI); NALCO smelter; and a Chemical plant (Orichem). In addition, coal mines and other mining activities are also predominant. Besides, there are 35 small-scale industries near existing major industries. The major plants along with their products, raw materials used and potential of liquid waste generated and volume coal fly ash generated are given in Table 1 [9].

The indiscriminate disposal of effluents due to industrial activities has completely unbalanced the pristine river environment, which has been silted due to large deposits of suspended solids.

2.3. Literature review

There are reports on coal fly ash characterization [2] of dissolved and particulate heavy metals in water [10] and fluoride in groundwater [8] and trace element distribution of river sediments of Orissa including the Brahmani River [7]. No study has been carried out so far to assess the behaviour and characteristics of heavy metals in the sediments of the Brahmani and Nandira Rivers using mineralogical, morphological, sequential leaching technique as well as statistical interpretation. The quantification of metal pollution through different indices like enrichment ratio, geo-accumulation index and pollution load index were determined in Brahmani and Nandira sediments Rath et al. [11]. But in the present study geochemical fractionation of metals in the said river sediments was determined and their potential ecological risk to the aquatic system was assessed using risk assessment code. RAC is a technique to evaluate metal bioavailability in aquatic system on a semi quantitative approach. A comparative chart is given in Table 2 [12–14,1,15–17] for the different methods adopted for quantifying metal pollution by different authors.

2.4. Objectives

The objectives of the study are to establish the provenance, distribution pattern of major and minor elements, association of metals in different geochemical phases, mineralogical and morphological characteristics of sediments and coal fly ash for identifying the sources. Further, the multivariate approach (factor and cluster) has been applied to understand the geochemical processes and to evaluate the responses occurring in the environment.

3. Materials and methods

3.1. Sample collection and analytical methods

The monitoring network and sampling strategy were designed to cover a wide range of determinants at key sites, which reasonably represent the sediment quality of the river systems accounting for tributary and inputs from industrial drains that have impact on downstream sediment quality. Under the sediment quality-monitoring Programme of the Brahmani River, samples from thirteen locations of Brahmani River (B1–B6) and Nandira River (N1–N7) were collected as shown in Fig. 1. Samples were collected at 0–20 cm depths manually by inserting a PVC tube (5 cm diameter) into the riverbed and removing it slowly. The core sediments were divided into 0–10 cm and 10–20 cm depth intervals for analysis. The sediment samples were homogenized and air-dried at room temperature. A portion of the sample was taken for textural analysis (Sand, Silt and Clay percentages).

Concentrations of metals like Al, Ti, Fe, Mn, Co, Cu, Cr, Ni, Pb, Zn, Cd and Hg were analyzed in bulk sediments. Powdered samples were digested in triplicate, in 100 ml Teflon beakers followed by addition of 2 ml $HClO_4$, 12 ml HF and 8 ml HNO_3. The concentration of metals was determined by AAS (Varian, Model Spectra 20+) in flame mode and that of Hg was determined in flameless mode with background correction. For Hg, sediments were digested for 2 h with aquaregia (HNO_3:3HCl) to which 5% $KMnO_4$ and potassium persulphate solutions were added [18]. All the samples were analyzed in triplicate with blanks similarly treated for metal analysis. The precision and accuracy of the methods were systematically and routinely checked by analyzing USGS reference samples like GXR (soil), where the precision (coefficient of variation of five replicate analysis) was 3% for Cu, Cr and Fe and 4% for Pb, Cd, Co, Ni, Mn and Zn.

Trace metals (Fe, Mn, Co, Cu, Cr, Ni, Pb, Zn, Cd) were sequentially extracted from <88 μm (-200ASTM) fraction of sediments of Brahmani and Nandira Rivers following the method proposed by Tessier et al. [19] into five phases operationally defined as exchangeable (F_1), carbonate (F_2), Fe–Mn hydroxide (F_3), organic (F_4) and residual (F_5). The <88 μm fraction contains fine sand, silt, and clay which are